

This paper describes the construction of a detailed gas-phase mechanism for tropospheric DMS photooxidation and its evaluation against a useful set of chamber observations. Such chamber datasets are extremely useful for evaluating commonly used chemical mechanisms, such as the Master Chemical Mechanism (MCM). The resultant model also includes limited heterogeneous chemistry of some semi-volatile DMS photooxidation products, which seems to improve the agreement between model and measurements. Detailed isoprene chemistry has also been incorporated into the model along with the DMS chemistry and evaluated against chamber data.

The broad conclusions from this paper are that the model does a reasonable job of simulating the DMS experimental data, which is further improved by the inclusion of heterogeneous chemistry. The presence of isoprene seems to enhance the production of certain DMS products, which are not well predicted by the model. Some discussion of possible explanations for this discrepancy is given.

The work in this paper is useful and the compiled mechanistic data can be used by the community for the modeling of DMS chemistry. I would have, however, liked more detailed discussions of the methodologies applied, in particular more details on the heterogeneous chemical modeling, and more discussion of the results and atmospheric implications/further work required. I would recommend this work be published once the following issues have been addressed.

Specific Comments

Manuscript would generally benefit from a quick overview of the written (scientific) English.

(1) Kinetic database (3.1.1): The comprehensive kinetic database is given in the supplementary section. It is interesting to note that the authors use the detailed isoprene chemistry from the latest version of the Master Chemical Mechanism (<http://mcm.leeds.ac.uk/MCM>). However, they seem to have not used or even referenced the comprehensive semi-explicit DMS chemistry also available in MCMv3.2. It would have also been a useful test of the MCM if its DMS chemistry were evaluated in the model against the chamber data. It is also strange that although the authors do briefly acknowledge the 2006 Chemical Review on dimethyl sulfide and dimethyl sulfoxide chemistry by Barnes et al., (106, 940-975), they do not reference it further and seem to not make that much use of the detail information available in this comprehensive review.

(2) Description of heterogeneous chemistry (3.1.2): More detail is required on the partitioning methodology applied. How did you exactly calculate/estimate K_p (Pankow, Kamens etc.)?. What are the values of k_{ad} and k_{des} you calculate? The chemical nomenclature in this section is also very confusing; Kinetic equations need to be written in a mathematical form. In what context are you using "@"?

(3) DMS photooxidation with coexisting isoprene (3.3.2): This title doesn't really make sense to me, I would re-word it "DMS photooxidation in the presence of isoprene". It is unclear to me what the motivation is of using isoprene as the co-reactant VOC, apart from the fact someone else has seen isoprene can effect DMS oxidation indoors. Would be good to discuss why isoprene in context in the introduction.

In section 3.3.2 the authors mainly focus on the fact that model under predicts MSA under high isoprene conditions, there is little discussion on the fact that the model molar yields of H₂SO₄ are consistently under predicted by a factor of 2 for all concentrations of isoprene. A plausible explanation for this under prediction could be that during the photooxidation process, a significant amount of ozone is produced, which can react with isoprene and its unsaturated products, such as MVK and methacrolein. The ozonolysis reaction forms excited Criegee Intermediates (CI) which can be stabilized (SCI) and react in a bimolecular manner with species such as H₂O and SO₂. These reactions are described in the MCMv3.2 isoprene chemistry, with the reaction with H₂O being dominant. However, Welz et al., (Science 335, 204 (2012)) have recently been able for the first time to measure the (upper limit) rate constants for the reaction of the CH₂OO SCI with a number of important atmospheric species, concluding that reaction with NO₂ and SO₂ is fast (very fast in the latter case) leading to the formation of SO₃ (i.e. H₂SO₄). It would be interesting to see the effect of the new rate data from Welz et al., (assuming the CH₂OO + SO₂ rate constant can be generalized to other SCIs) has in the isoprene/DMS model.

Other Comments:

P14671, line 16: The authors refer to the "updated mechanism" – updated from what? Please give reference to previous work

P14672, line 25: MCM need proper referencing throughout the manuscript (see website: <http://mcm.leeds.ac.uk/MCM/citation.htm>): website and most recent protocol (Saunders et al., Atmos. Chem. Phys., 3, 161–180, 2003).

P14673, Experimental procedures: what was the reasoning for the RH levels used? How was water injected into the chamber and RH maintained throughout the experiment?

How is chamber dilution accounted for?

Do you take into account chamber wall reactions (apart from wall losses)? It is well known that irradiated Teflon chambers suffer from:

- (1) The introduction of free radicals from heterogeneous wall reactions
- (2) (Light dependent) adsorption/desorption of NO_y species (including HONO) to/from the chamber walls
- (3) The off-gassing of various reactive species from the chamber walls, which can contribute significantly to the radical budget of the system and subsequent ozone formation

See Rickard et al., (Atmospheric Environment 44 (2010) 5423–5433 2010) and references therein.

P14673, line 6: “evaluate”, not “validate”.

P14675, line 16: “existing explicit model for DMS” – what model? Reference?

P14675, line 21: “semi-volatile” gaseous DMS products.

P14677, line 11: What does “PAR-NIR and UV-PAR, Apogee” mean?

P14679, line 1: Again, reference “existing” models.

P14680, line 24: the H₂SO₄ model and measurement profiles are difficult to see. Whilst NO is well simulated, NO₂ is certainly not in the latter stages of all experiments, glyoxal also not that well simulated (why?)

P14681, line 18: How important are O(³P) reactions with organics in the “real” atmosphere?

P14682, line 25: It is not that surprising that SO₂ profiles are simulated well as the authors “fit” the model so that they are in good agreement!

P14683, line 3: MSA production appears to increase “in the presence of isoprene”.

P14683, line 12: This sentence does not make any sense!

Table 1: Give speciated initial NO_x (i.e. NO and NO₂) concentrations in the table.

Table 3: A graphical representation of the differences between model and measured molar yields of MSA and H₂SO₄ would be useful to the reader. In footer legend, “Table 3” should read “Table S3”.

Fig 1; DMSO-1 Profile A: DMSO line should read “DMSO2 (E)”

Supplementary Material: For consistency, put the DMS chemistry tables before DMSO. In the table footers, explain how you estimated the rate constants.

The correct mathematical way of giving an Arrhenius expression in the tables should be, e.g: $1.13\text{E-}11*\text{EXP}(-254/\text{TEMP})$ – thereby a computer model or spreadsheet can directly interpret the rate expression. Note all other rate constants given are for 298K and 1 atm (otherwise give the full temperature and pressure dependent rate expressions).